METHODS FOR THE OXIDATION OF POTASSIUM MANGANATE

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METHODS FOR THE OXIDATION OF POTASSIUM MANGANATE

A THESIS

PRESENTED BY

FRANK R. JOHNSON AND ALBERT PEARSON

TO THE

PRESIDENT AND FACULTY

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FOR THE DEGREE OF

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IN

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INTRODUCTION

The work described in this paper is the result of suggestions made by Prof. H. Mc Cormack, and has been carried out as outlined by him and by Prof. C. A. Tibbals. At the outset it was the intention of the authors to investigate the electrolytic oxidation, using manganese or ferro-manganese electrodes, and in that way convert all the potassium into potassium permanganate. This part of the work had to be dispensed with on account of the inability to obtain the electrodes. Since the time that could be devoted to this work amounted to only about four hours a day for a period of one month the investigation of the subject is by no means complete, but only the high spots have been touched upon. Almost an unlimited number of differing conditions, especially in the electrolytic oxidation, could have been obtained, such as, varying current density, varying temperature

of electrolyte, and electrodes of different materials. No great accuracy in the analytical work is claimed, due to the unstability of the material used. Rapid analyses were made frequently in connection with the experiment in order that the results might be correctly interpreted.

The object of this work was to examine the methods used, and to find a method by which potassium manganate may be oxidized to potassium permanganate without loss of potassium hydroxide or manganese. The potassium manganate must be dissolved in caustic potash solution since it is not stable in neutral or acid solution. By the ordinary methods of oxidation in which sulphuric acid, carbon dioxide and chlorine are used, or by boiling a weakly alkaline solution, either part of the manganese is precipitated as manganese dioxide which, of course, decreases the yield of permanganate, or the potassium hydroxide in ex-

cess will be converted into chloride or carbonate, the caustisizing of which is an expensive process. By means of ozone all the manganese may be converted into permanganate and the excess potassium hydroxide is left as such. This is evidently the object sought, but the process cannot be used commercially on account of the high price of ozone.

The importance of the subject from a commercial point of view will at once be apparent when the enormous increase in price, since the outbreak of the European War, is noted. In July 1914 potassium permanganate sold at 10¢ a pound, in July 1915 at 70¢ a pound, in July 1916 at $1.75 a pound, in July 1917 at $4.00 a pound. At the present date the price is about $4.00 a pound. This tremendous rise in price is due chiefly, first to the advance in price of potassium hydroxide, secondly to the fact that its manufacture has not been developed in this

country. Before the war nearly all potassium permanganate used in this country was imported from Germany.

The literature relating to the subject is extremely limited. The only descriptions the authors were able to find at the best libraries in Chicago were those given in text books on chemistry, all of which contain only the common methods of manufacture with theoretical chemical equations. A German patent was taken out in 1898 for the electrolytic oxidation of potassium manganate, but no details of the process are available.

The authors wish to express their thanks to Prof. McCormack and Prof. Tibbals for helpful suggestions and information throughout this work.

PART - 1

CHEMICAL OXIDATION

Standard Solutions:- A potassium permanganate solution containing approximately 31.6 grams of the salt per liter was made up and allowed to stand for a period of about two weeks. It was then standardized with sodium oxalate in acid solution. The average of a number of titrations gave the following standard:

1 c.c. $KMnO_4$ contains .00342 grams $KMnO_4$.

A nearly concentrated solution of ferrous ammonium sulphate was then prepared. A ratio between this solution and the permanganate solution was then obtained giving as an average value the following:

1 c. c. $KMnO_4$ = .156 c. c. $FeSO_4$

1 c. c. $FeSO_4$ = 6.41 c. c. $KMnO_4$

This gives 1 c.c. $FeSO_4$ = .0219 grams $KMnO_4$

From the relation that 2 $KMnO_4$ = $FeSO_4$

we get that 1 c.c. $FeSO_4$ contains .1055 gr.$FeSO_4$

That is 1 c.c. $FeSO_4$ = .0219 grams $KMnO_4$.=

.0076 grams Mn when used on $KMnO_4$.

$2\ FeSO_4 + MnO_2 + 2\ H_2\ SO_2 =$

$Fe_2(SO_4)_3 + MnSO_4 + 2\ H_2O$ (Eq.1)

From this relation we get

1 c.c. $FeSO_4$ = .0191 grams Mn when used on MnO_2

$K_2MnO_4 + 4FeSO_4 + 4H_2SO_4 =$

$K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3$ (Eq.2)

From this relation we get

1 c.c. $FeSO_4$ = .0333 grams K_2MnO_4

$\frac{KMnO_4}{Mn} = 2.88$

$\frac{K_2MnO_4}{Mn} = 3.95$

Preparation of Solution #1:- The material consisted of K_2MnO_4, containing about 5% MnO_2 was covered and saturated with a solution of KOH. It was supplied by Prof. McCormack.

The crystals were centrifuged and dried at a temperature of about 150 deg. centigrade. 40 grams of this material was dissolved in a 5% KOH solution, filtered, and the filtrate was then made up to 1000 c.c. This solution will be referred to as Solution #1.

Stability Test of Solution #1:- The first stability test was made as follows:- In each of 10 250 c.c. Erlenmeyer flasks was placed 50 c.c. of water. To flask #1 was added 50 c.c. of solution #1, to #2 was added 45 c.c. etc., as shown in Table #1. These samples were allowed to stand nine days, unstoppered, at room temperature. At the end of this time they were filtered through asbestos in Gooch crucibles. The residue of MnO_2 was dissolved in ferrous sulphate solution, and the excess ferrous sulphate was then titrated with standard permanganate solution. To the filtrate was added an excess of ethyl alcohol. It was heated to boiling temperature,

the MnO_2 was filtered off, dissolved, and titrated as above. The Mn precipitated on standing and the Mn left in the solution was calculated from the amount of $FeSO_4$ used to dissolve the MnO_2. The object of the test was to determine the stability of K_2MnO_4 in 5% solution of KOH. It will be seen from the Table that as the concentration of KOH decreases the percentage of Mn thrown out of solution increases. The composition of the K_2MnO_4 may be represented by the following equation:-

$$3KMnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH \qquad (EQ.3)$$

According to the above equation the maximum Mn precipitated should not exceed one-third of the total. Referring to Table #1 it will be noted that more than the theoretical amount of manganese was thrown down. The discrepancy is probably due to incorrect analysis. The material was perhaps contaminated with $KMnO_4$ as a result of decomposition.

TABLE #1

NO.	Water c.c.	Sol.#1 c.c.	%KOH	Mn ppt.	Mn in sol.	%Mn ppt.
1	50	50	2.5	.029	.137	17.6
2	50	45	2.37	.034	.128	20.8
3	50	40	2.22	.028	.116	19.4
4	50	35	2.06	.028	.098	22.1
5	50	30	1.87	.031	.075	29.3
6	50	25	1.67	.027	.058	31.4
7	50	20	1.43	.028	.040	41.2
8	50	15	1.15	.026	.027	49.0
9	50	10	.84	.015	.019	43.5

Oxidation by Neutralization and by Boiling:-
Solution #1 was employed in the following tests. In each case a sample was prepared, and the reaction allowed to take place in a 250 c.c. Erlenmeyer flask.

Samples #1 and #2 were prepared by adding 10 c.c's of 10% sulphuric acid to 50 c.c. of solution #1, nearly neutralizing the excess of potassium hydroxide. They were then heated to the boiling point, and held at that temperature for ten minutes. They were then filtered through asbestos in Gooch crucibles. The residue of MnO_2 was dissolved in $FeSO_4$ solution, the excess of which was then oxidized by the standard $KMnO_4$ solution.

Samples #3 and #4 were boiled one hour without the addition of acid, they were then filtered and titrated as above.

Samples #5 and #6 were boiled for one hour with the addition of 5 c.c's of 10% sul-

phuric acid, after which they were filtered and titrated as in the previous cases.

Samples #7 and #8 were boiled thirty minutes without the addition of acid. They were then filtered and titrated.

Samples #9 and #10 were treated as follows: Air was blown through the cold solution for twenty minutes. No perceptible change was observed. Solution was then heated to boiling temperature, and air was passed through for twenty minutes, at the end of which time oxidation seemed to be complete by the prevelance of a deep purple color of the solution.

The results of the experiments are shown in Table #2. The chemical reactions are represented by equation 3 on Page 9. According to the equation referred to above one-third of the total Mn should have been precipitated as MnO_2. In computing the figures in Table #2 it was assumed that all the Mn was present

TABLE #2

Sample No.	Sol.#1 c.c.	Mn ppt.	Mn as $KMnO_4$	%Mn ppt.
1	50	.076	.122	38.4
2	50	.076	.125	38.3
3	50	.076	.147	34.1
4	50	.038	.167	20.7
5	50	.061	.157	28.0
6	50	.061	.157	28.0
7	50	.033	.160	17.1
8	50	.033	.160	17.1
9	50	Lost	Lost	Lost
10	50	.024	.162	12.9

in solution as $KMnO_4$. This accounts for the fact that in some cases the percent Mn precipitated is less than one-third of the total.

Oxidation with Carbon Dioxide:- (preliminary) Sample #11 was treated in the following manner: Carbon dioxide was passed through 50 c.c's of solution #1 in the cold state for thirty minutes. It was then filtered and titrated in the regular way.

Sample #12 was treated as #11 with the exception that the solution was kept at the boiling temperature while the carbon dioxide was passed in.

TABLE #3

Sample No.	Sol.#1 c.c.	Mn ppt.	Mn as $KMnO_4$	%Mn ppt.
11	50	.045	.154	22.6
12	50	.046	.151	22.4

Solubility Determination:- A saturated solution of K_2MnO_4 was made by dissolving as much of the salt as possible in a 10% solution of KOH, the solvent being somewhat above room temperature. This solution was then filtered through asbestos, and 50 c.c's of it was collected in a dried and weighed beaker. The solution in the beaker was then evaporated to dryness, and dried in an oven at 120 deg. centigrade. The residue and the beaker were then weighed and the weight of the residue was obtained by difference.

Another saturated solution was prepared in the same manner using a 5% solution of KOH. The weight of the residue was obtained as in the previous case.

Weight of residue from 10% KOH sol. = 23.0 gr.

Weight of residue from 5% KOH sol. = 22.4 gr.

The solubility of K_2MnO_4 in 10% KOH = 460 gr./l.

The solubility of K_2MnO_4 in 5% KOH = 448 gr./l.

Preparation of Solution #2:- This solution was prepared by dissolving 500 gr. of the material in 2500 c.c. of 10% KOH solution. This solution was filtered, and the residue of MnO_2 was dried and weighed.

Weight of MnO_2 filtered off = 65.6 gr.

Upon dissolving the salt potassium permanganate crystals were found to separate out while the solution was concentrated, proving that the material contained a considerable amount of $KMnO_4$. This solution will be used in all subsequent experiments.

Oxidation with Carbon Dioxide:- Samples #13 and #14, each of 25 c.c's, were prepared as follows: Carbon dioxide gas was passed through the boiling solution fifteen minutes. The flask was heated on a wire gauze over a Bunson flame. The reaction took place in 2 50 c.c's Erlenmeyer flasks. The oxidized samples were then filtered, the MnO_2 and the solution were titrated in

the ordinary way.

Sample #15 was treated like the last two, with the exception that CO_2 was passed through the heated solution for six minutes only.

Sample #16 was treated like the previous samples, excepting that twelve minutes was allowed for the oxidation. The results of the experiments are shown in Table 4.

TABLE #4

Sample No.	Sol.#2 c.c.	Mn ppt.	Mn as $KMnO_4$	%Mn ppt.
13	25	.116	.276	29.6
14	25	.107	.275	28.0
15	25	.091	.284	24.3
16	25	.102	.275	27.1

From an inspection of the Table it will be noted that in no case is one-third, or the theoretical amount, of the total Mn precipitated. This is explained by the fact that some of the Mn in the sample was in the form

of $KMnO_4$ before the oxidation which, of course, will decrease the amount which would otherwise have been precipitated. It will also be seen that sample #15 was not completely oxidized due to lack of time.

Oxidation with Chlorine:- A chlorine generator was prepared by means of inserting a separatory funnel through a stopper into a 500 c.c. flask. A glass tube led from the flask through the stopper into a small wash bottle, containing a small amount of water. This tube extended below the surface of the water so that the gas was forced to bubble through, thus removing any HCl which might be carried over. Only a small volume of water was used in order to make the loss of chlorine as small as possible. The gas was led from the wash bottle to a T-tube, one end of which connected to a beaker contain-

ing a little KOH solution, the other branch was connected to a glass tube which could be immersed in the solution to be oxidized. The chlorine was prepared by means of placing one-half pound bleaching powder in the flask and allowing hydrochloric acid to trickle down upon it from the separatory funnel. The reaction was carried out in 50 c.c. parting flasks, so as to make the body of solution as deep as possible.

Sample #18 was treated as follows: 25 c.c's of solution #2 was used, as shown in the Table. Chlorine was passed through the cold sample for two minutes. This oxidized sample was then filtered and the residue of MnO_2 titrated. The filtrate was oxidized by the addition of ethyl alcohol, heated to boiling temperature, and filtered. The resulting MnO_2 was then titrated in the ordinary way. The amount of Mn precipitated and that converted into $KMnO_4$ was calculated from the amount of $FeSO_4$ used.

Sample #19 was treated as #18, the only difference being that Cl was passed through for a time of four minutes.

Sample #20 was treated in every respect like #19.

Sample #21 was oxidized with alcohol, without the application of Cl.

The results of the experiments are shown in Table 5.

In the oxidation by this method it was necessary to reduce the $KMnO_4$ to MnO_2 and then titrating the MnO_2 which represents the total Mn present. The necessity of this is shown by sample #17 which if calculated as previously would give a much greater amount of total Mn than was present in the original sample.

When chlorine is passed into a solution of K_2MnO_4 containing an excess of KOH the following reactions take place.

$K_2MnO_4 + Cl = KMnO_4 + KCl$ (Eq.5)

$KOH + 2Cl = KOCl + HCl$ (Eq.6)

When the resulting solution is titrated with $FeSO_4$ the KOCl acts as an oxidizing agent on the $FeSO_4$ as shown by the following equation:

$$2FeSO_4 + KOCl + H_2SO_4 = Fe_2(SO_4)_3 + KCl + H_2O \quad \text{(Eq.7)}$$

TABLE #5

Sample No.	Sol.#2 c.c.	Mn ppt.	Mn as $KMnO_4$	%Mn ppt.
17	25	.0009	.372	.24
18	25	.0011	.386	.28
19	25	.0009	.325	.27
20	25	.0008	.356	.20
21	25	00000	.376	---

It will be seen from Table #5 that practically all the Mn present in the sample has been converted into $KMnO_4$. This is in accordance with theory as shown by equation 5.

PART - 2

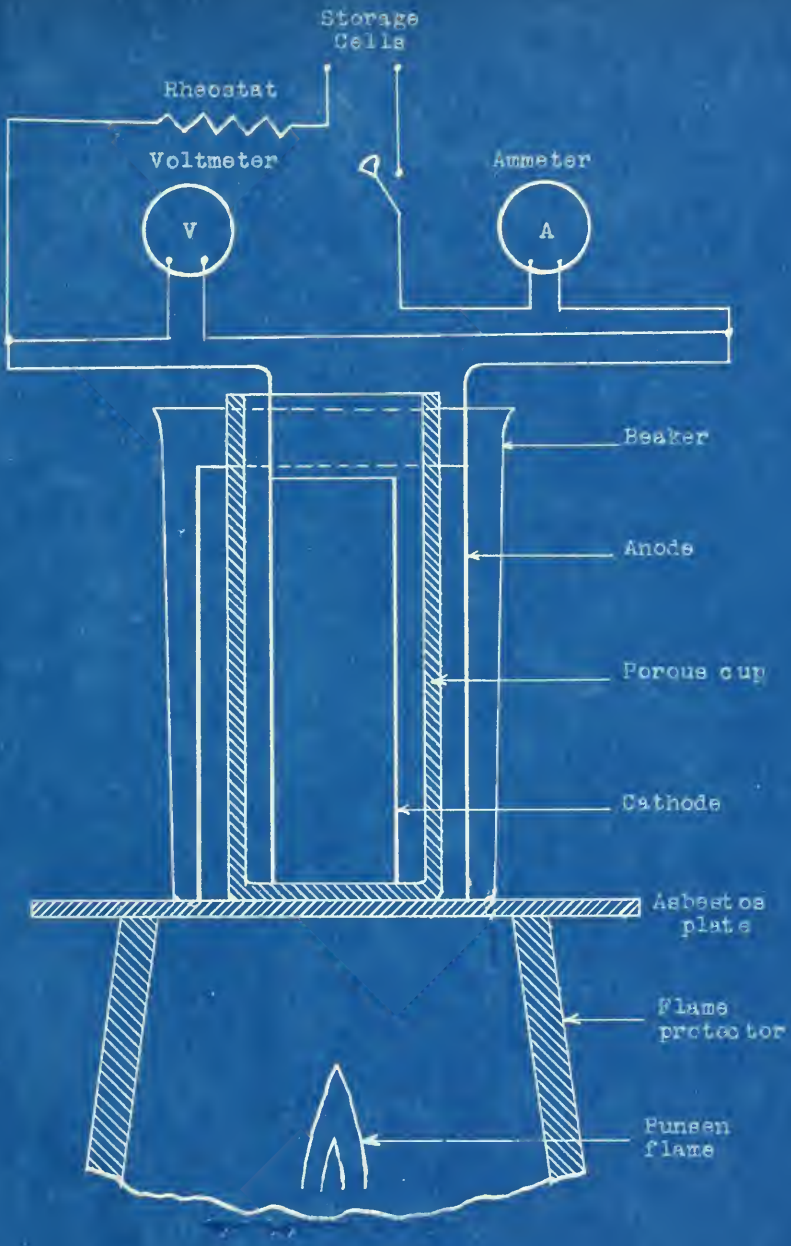
ELECTROLYTIC OXIDATION

A vertical section of the electrolytic cell used is shown in the figure opposite page 24. A tall narrow beaker was used in order that a small sample, and yet a relatively large anode area could be obtained. The porous cup was used as a diaphragm.

A platinum anode was used in the first trial, but it was abandoned, since iron could be used just as well. Iron electrodes, both anode and cathode were then used in all the experiments. The electrodes were cleaned by placing them in a dilute solution of sulphuric acid for a few moments before immersing them in the sample.

The electrical equipment consisted of a Weston 0 - 25 voltmeter, a Weston 0 - 25 ammeter, a carbon block rheostat, switches, wires, and clamps as required.

In the first test, sample #1, the platinum anode was placed in the porous cup but in subsequent tests the anode was placed outside the cup, thereby making the anode area greater than the cathode area. A constant current of 5 amperes was used in all the runs. The voltage across the cell was measured every two minutes during a run and the average computed. The time of flow of the current and the temperature of the electrolyte were also recorded. Before a run was started the porous cup was saturated with K_2MnO_4 solution so as to make the loss due to absorption of the measured sample as small as possible. The levels of the liquids inside and outside the cup were kept at the same height in order to prevent leakage from one into the other.



Electrolytic Cell

Solution #2 was used without dilution throughcut the experiments. Stirring was done by means of moving the anode slowly and frequently.

When a sample had been oxidized it was diluted to 1000c.c's after being allowed to stand for a short time so that an examination for MnO_2 could be made. 100 c.c's were then drawn from the oxidized sample and were titrated with $FeSO_4$. The corresponding amount of Mn was calculated. Another 100 c.c's were then oxidized by alcohol and the total Mn determined in the ordinary way.

The electrodes were cut out from sheet iron and the areas of each immersed was as follows:

Anode area = 150 sq. cm.
Cathode area = 70 sq. cm.

Samples #1 and #2 were treated as follows: To 10 c.c's of solution #2 was added an excess ethyl alcohol. The solution was then heated

to boiling temperature, filtered, and the resulting MnO_2 was titrated as before. From this the total Mn present in 10 c.c's of the unoxidized sample was calculated. The values of Mn in Table #6 were calculated, for 25 c.c. samples, so as to be comparable with values in the other Tables.

Sample #3, of 100 c.c's of solution #2, was treated in the following manner:
A current of 5 amp. was passed through the solution for thirty minutes. The temperature of the electrolyte at the beginning of the run was 28 deg. centigrade. At the end of the run the temperature of the liquid in the anode compartment was 48 deg. centigrade, the rise in temperature being due to the current alone. As stated above this was the only sample on which a platinum electrode was used. The anode area in this case was fifty square centimeters.

Sample #4 was treated like #3 excepting

that both electrodes were of iron and the anode was placed outside the porous cup.

Samples#5, #6, #7, #8 and #9 were all treated as #3, with the exception that the temperature was kept at 50 deg. centigrade throughout the oxidation period, and the time of oxidation was varied as shown in Table #6.

The results of the experiments are shown in the Table below:

TABLE #6

Sample No.	Volts	Amp.	Mn as K_2MnO_4	Total Mn	Time min.
1	-----	---	------	.370	----
2	-----	---	------	.365	----
3	3.6	5	.375	.344	30
4	3.4	5	.375	.373	30
5	2.6	5	.375	.368	10
6	2.6	5	.350	.374	6
7	2.6	5	.368	.380	10
8	2.6	5	.370	.370	12
9	2.6	5	.369	.374	8

The column headed Mn as $KMnO_4$ is the Mn from 25 c.c's of solution #2 calculated from the standard, 1 c.c. $FeSO_4$ = .0076 gr. Mn (see page 6). The column headed total Mn is the toal Mn in the unoxidized or oxidized samples as the case may be.

It was found that approximately 50 deg. centigrade was the temperature at which the lowest voltage was required to produce a given current. This temperature was therefore used in all remaining experiments. When a current is passed through a solution of a salt oxygen, or its equivalent is liberated in the nascent state at the anode. The oxidation of the $KMnO_4$ is brought about by this oxidizing agent which in this case is the OH-ion. The potassium ion travels to the cathode where it combines with water to form potassium hydroxide.

Second Stability Test:- Four nearly concentrated solutions were made up containing varying amounts of KOH as shown in the Table below. The samples were all held at a temperature of 60 deg. centigrade for thirty minutes. It is assumed that this amount of time is ample for carrying out the oxidation electrolytically on a commercial scale. Samples were then filtered, the residue of MnO_2 titrated. Filtrate was then oxidized with alcohol, heated to boiling temperature, and filtered. The resulting MnO_2 was titrated and the total Mn in filtrate was calculated. The results are shown in Table #7.

TABLE #7

Sample No.	%KOH	%Mn ppt.
1	10	.15
2	7.5	.18
3	5	.29
4	2.5	.38

PART - 3

DISCUSSION and CONCLUSION

Part 1 of this work presents nothing new, since the methods of oxidation used are those used in practice in this country today. The object of the experiments was to obtain some data on the efficiency of the different processes.

In the first stability test the strongest KOH solution contained only 2.5% KOH. It will be noted that the K_2MnO_4 in this concentration of KOH decomposed rather rapidly. It was therefore necessary to make a solution, to be used in the experiments, strong enough in KOH so as to keep the samples fairly stable during the time of the tests. Solution #2

was, therefore, made up from 10% KOH, and it was found to remain very nearly constant during the time in question.

Since the electrolytic oxidation was made in a hot solution it became necessary to determine the stability of this solution at that or a somewhat higher temperature. From the results of the second stability test it is evident that for the short period of time required for the oxidation the K_2MnO_4 could be dissolved in a dilute solution of KOH without appreciable loss of Mn.

By comparing Table #2 and #3 we find that the average percentage Mn precipitated is the same. This is also true theoretically. Since the same amounts of Mn is precipitated, oxidation by boiling is the more desirable of the two, because the excess of KOH is left in the solution unaltered.

In the oxidation with chlorine it will be seen from Table #5 that only about one-

fourth of 1% Mn is precipitated by decomposition. This process is evidently perfect as to the conversion of Mn, but the cost of Cl, and the loss of KOH as such, are two undesirable features of the process. The loss of KOH is, of course, extremely important while KOH remains at its present price.

From an examination of Table #6 it is at once apparant that by the electrolytic oxidation all the Mn in the sample has been converted into $KMnO_4$, except in sample #6 in which the time allowed was probably not sufficient. It will also be seen from Table #6 that a time of from eight to ten minutes is sufficient for the completion of the oxidation.

As to cost of oxidation by the electrolytic method we may make the following estimation: Let us consider Sample #5 which seems to be an average of the values in the tables, and estimate the cost per pound of

$KMnO_4$, assuming that electrical energy is 7¢ per K.W.H.

25 c.c. of solution #1 = .375 gr. Mn

100 c.c. of solution #1 = 1.5 gr. Mn

1.5 gr. Mn = 4.31 gr.$KMnO_4$ = 100 c.c. sample.

Electrical energy used = $\frac{2.6 \cdot 5. \cdot 10}{1000 \cdot 60}$ = .00217 K.W.H.

4.31 gr. = .0095#

1# $KMnO_4$ requires $\frac{.00217}{.0095}$ = .228 K.W.H.

At 7¢ per K.W.H. for electrical energy the oxidation of 1# $KMnO_4$ would cost 1.6¢

It is obvious that a commercial cell used for this oxidation would have a far greater efficiency than the experimental cell used in this work. The cost of oxidation could therefore probably be reduced to less than 1¢ a pound.

Even if the price of potassium permanganate should again come down to what it was before the war the electrolytic oxidation could be used profitably for the following reasons: The cost of electrical energy

is not prohibitive. The process could readily be made continuous. No evaporation would be necessary, since the permanganate is rather insoluble as compared with the manganate, the former crystallizes out and may be removed from the cell. Potassium manganate may be supplied constantly so as to keep the electrolyte nearly concentrated with it at all times.